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Purdue University  
Department of Physics

SEMICONDUCTOR RESEARCH  
FINAL REPORT

October 1, 1960 to September 30, 1961

Contract DA 36-039-sc-87394

between  
PURDUE RESEARCH FOUNDATION  
and  
UNITED STATES SIGNAL CORPS  
PRF 2641

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## SUMMARY OF RESULTS

### I. ELECTRICAL AND OPTICAL PROPERTIES

#### Energy Band Structure of Gallium Antimonide (W.M. Becker, A.K. Ramdas, and H.Y. Fan)

Resistivity, Hall coefficient, and magnetoresistance were studied for n- and p-type GaSb. The infrared absorption edge was investigated using relatively pure p-type, degenerate n-type, and compensated samples. Infrared absorption of carriers and the effect of carriers on the reflectivity were studied. The magnetoresistance as a function of Hall coefficient for n-type samples at 4.2°K gave clear evidence for a second energy minimum lying above the edge of the conduction band; the energy separation is equal to the Fermi energy for a Hall coefficient of 5 cm<sup>3</sup>/coulomb. The shift of absorption edge in n-type samples showed that the conduction band has a single valley at the edge, with a density-of-state mass  $m_{d1} = 0.52 m$ . By combining the results on the edge shift, magnetoresistance, and Hall coefficient, it was possible to deduce: the density-of-states mass ratio  $m_{d2}/m_{d1} = 17.3$ , the mobility ratio  $\mu_2/\mu_1 = 0.06$ , and the energy separation  $\Delta = 0.08$  ev between the two sets of valleys at 4.2°K. Anisotropy of magnetoresistance, observed at 300°K, showed that the higher valleys are situated along <111> directions. The infrared reflectivity of n-type samples can be used to deduce the anisotropy of the higher valleys; tentative estimates were obtained. Infrared reflectivity gave an estimate of 0.23 m for the effective mass of holes. The variation of Hall coefficient and transverse magnetoresistance with magnetic field and the infrared absorption spectrum of holes showed the presence of two types of holes. Appreciable anisotropy of magnetoresistance was observed in a p-type sample, indicating that the heavy hole band is not isotropic; this was confirmed by the infrared absorption spectrum of holes. The results on the absorption edge in various samples seemed to indicate that the maximum of the valence band is not at  $k = 0$ . However, it appears likely that transitions from impurity states near the valence band produced absorption beyond the threshold of direct transitions.

#### Galvanomagnetic Measurements on III-V Compounds (W.M. Becker and H.Y. Fan)

Investigation of the band structure of p-InSb was undertaken using Hall coefficient, resistivity, and magnetoresistance measurements. The behavior of the Hall coefficient and transverse magnetoresistance with magnetic field at 77°K indicated the presence of two types of holes. Magnetoresistance anisotropy was observed suggesting that the heavy hole band in InSb is not isotropic.

A similar type of investigation initiated on p-AlSb gave only a weak dependence of Hall coefficient and transverse magnetoresistance on magnetic field at 77°K. Preliminary measurements show anisotropy in the magnetoresistance.

## Electronic Transport Properties of P-Type Germanium at Low and High Electric Fields

(D.M. Brown and R. Bray)

The following summary is the abstract from the Ph. D. Thesis of D. M. Brown, completed during the past year.

Scattering of holes in p-type germanium by acoustical and optical phonons and impurities has been studied over a wide range of sample temperatures and impurity concentrations. This has been done for low D.C. fields where the conductivity is ohmic and also in the high field region where the conductivity is a rapidly varying function of the applied electric field. All the high field measurements were made with short voltage pulses to prevent sample heating.

The analyses were based on two paraboloidal bands of different effective masses centered at  $k = 0$  and taken into account by assuming that (1) the lattice scattering relaxation time is the same for heavy and light holes and (2) ionized impurity scattering is limited to intraband transitions.

The mobility in relatively pure samples (lattice scattering dominant) was studied to determine whether a  $T^{-3/2}$  relationship, characteristic of simple acoustical mode scattering, exists for lattice mobility at low temperatures. The magnitude of the mobility was found by using it as the only adjustable parameter. In the range  $15^{\circ}\text{K} \leq T \leq 70^{\circ}\text{K}$ , excellent fit to the data could be obtained with calculations based on a lattice mobility  $\mu_{ac}^L = 580,000 (T/15 \text{ K})^{-3/2} \text{ cm}^2/\text{v-sec}$ , and an ionized impurity mobility given by the Brooks-Herring formula. An empirical test of the range of validity of the Brooks-Herring formula was made on a group of samples with concentrations as high as  $10^{17}/\text{cc}$ . At  $T \geq 90^{\circ}\text{K}$ , the usual  $T^{-2/3}$  temperature dependence of lattice mobility is observed. In fitting this data above  $90^{\circ}\text{K}$ , the only adjustable parameter was the ratio of the optical to acoustical mode coupling constants,  $(\xi_{op}/\xi_{ac})^2$ , for which a value of 3.8 was obtained.

The high field measurements were intended to clarify the role of optical and acoustical mode lattice scattering and impurity scattering in determining the carrier mobility and carrier energies at high fields. Oriented samples were used throughout. For most of the analyses, it was useful to assume a Maxwell-Boltzmann distribution at a carrier temperature  $T$  greater than that of the lattice temperature  $T_L$ . At  $T_L$ 's  $< 77^{\circ}\text{K}$  where acoustical mode scattering is dominant at low fields, a hot carrier mobility theory based only on acoustical mode interactions is in excellent agreement with the experiments, at low and high fields. The treatment at low fields substantiates the conclusion that the intrinsic mobility at low temperatures is determined by simple



acoustical phonon scattering. Inclusion in the theory of the expected optical phonon scattering at  $T_L \geq 77^\circ\text{K}$  or at  $E > 60 \text{ v/cm}$  at all temperatures makes the agreement appreciably poorer, but yields low and more reasonable carrier temperatures at high field strengths.

Additional experiments were designed to test the validity of the temperatures predicted by the different lattice scattering models. These experiments included studies of (1) the effect of ionized impurity scattering on hot carriers, (2) steady state ionization of shallow and deep lying impurity levels (Ga, and Cu and Zn), and (3) intrinsic ionization at very high field strengths. The conclusion is that the lower temperatures estimated by including optical phonon scattering must be more nearly correct. The failure of the theory, in this case, to fit the field dependence of the mobility at high field strengths may be due to the fact that the band structure and scattering parameters can not be extrapolated from low energies (near  $k = 0$ ) to the very high energies encountered at high electric fields.

Fundamental differences in the steady state ionization of shallow and deep impurity levels by hot carriers were found. Deep acceptor levels generally exhibit no sudden breakdown, and ionization at high fields is incomplete. Shallow level ionization, at  $20^\circ\text{K}$ , is nearly the same at a given carrier temperature whether this temperature is produced by lattice or electric field heating. This implies that ionization and recombination processes for shallow acceptors involve basically only carrier-carrier interactions. For deep levels, it is concluded that the ionization by impact is relatively inefficient, and that recombination may involve predominantly phonon processes.

#### Anisotropy of Hot Carriers in Germanium (D. Deutsch and R. Bray)

The following summary is the abstract from the M. S. Thesis of D. Deutsch, completed during the last year.

At low electric field, when the carriers are nearly in thermal equilibrium with the lattice, the mobility is constant and isotropic. At high field, the effective temperature of the carriers is raised above that of the lattice, and the mobility becomes both anisotropic and a function of the magnitude of the field. The dependence of the mobility on the magnitude of the field is due to the variation of relaxation time with carrier energy. The anisotropy of mobility can be attributed to the anisotropy of the constant energy surfaces of the conduction and valence bands of germanium. Since the effective mass is anisotropic, some directions of the applied electric field will be more favorable than others for energy gain by the carriers. Thus the effectiveness of the field in heating the carriers will depend on its direction of application, producing an anisotropy in the mobility of hot carriers. The anisotropic band

structure allows the existence of groups of carriers having different effective temperatures and thus different mobilities within the same band. The current contributions of these groups produce a total current which in general deviates from the direction of the applied field, resulting in a transverse field as measured by Sasaki, et al.

We have measured the anisotropy of mobility in p and n-Ge at 77°K for both pure and impure material. The anisotropy is qualitatively similar in p and n-Ge, although the degree of anisotropy is greater in n-Ge. We also find that the magnitude of the anisotropy is field dependent and reaches a maximum at intermediate fields. For p-Ge, the degree of anisotropy is the same for carrier concentrations of approximately  $2 \times 10^{13}$  and  $1 \times 10^{15}/\text{cm}^3$ . For given orientations of the field, the mobility of hot carriers in p-Ge is in no way dependent on carrier concentration, for the range investigated. In n-Ge, the degree of anisotropy may possibly depend on carrier concentration. For n-Ge, at high field the magnitude of the mobility in oriented samples depends on the carrier concentration although the slope of the mobility curve is the same for carrier concentrations of  $1.90 \times 10^{13}$  and  $1.50 \times 10^{15}/\text{cm}^3$ .

#### Hot Carrier Temperature from Infrared Measurements (W. Pinson and R. Bray)

Modulation of infrared (2-5  $\mu$ ) transmission through p-type Ge by heating the holes with pulses of high electric field has been observed. The objective of the experiment was to deduce the temperature of the hot carriers by comparing the changes in transmission due to the application of high fields with those produced by heating the whole crystal. The possibility of measuring hot carrier temperatures in this fashion is based on the assumptions: (1) that only the distribution function of the holes determines the infrared transmission; (2) that the hot carriers produced at high field strength have a Maxwellian distribution; (3) that the valence band structure does not alter with increasing lattice temperature. The first assumption is consistent with the present theoretical model of inter band infrared absorption in p-type Ge.

The overall consistency in the 2.0 - 5.0  $\mu$  range between the two sets of change of transmission data is not good. However, reasonable consistency is observed in the 2.8 to 4.0  $\mu$  range and forms the basis for the estimate of hot carrier temperature shown in Table I. The estimated temperatures in Table I are several times smaller than those derived from an analysis of the mobility of hot carriers, but seem to be higher than those measured by Paige and Brown<sup>1</sup> who have used an infrared technique similar to ours.

Table 1

Electric Field	Estimated Hot Carrier Temperature*	Estimated Change in Hole Temperature
180 volts/cm	105°K	25°K
350 volts/cm	130°K	50°K
570 volts/cm	145°-165°K	65°-85°K
770 volts/cm	160°-180°K	80°-100°K
1070 volts/cm	170°-190°K	90°-110°K

\* Lattice temperature of crystal = 80°K  
Carrier concentration =  $1.8 \times 10^{15}$  holes/cm<sup>3</sup>.

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1. M.A.C.S. Brown and E.G.S. Paige, Phys. Rev. Letters, Aug. 1, 1961.

Recombination Radiation in GaSb (I. Filinski and H.Y. Fan)

Measurements of recombination radiation in GaSb have been made using a pulse technique. The block diagram of the apparatus is shown in Fig. 1. Optical instead of electrical injection of minority carriers was used in the latest experiments. Using optical injection, one can work with homogenous samples. Also reabsorption of the recombination radiation is not as strong as in the case of injection through a p-n junction.

Samples of p-type GaSb, compensated p-type, degenerate p-type and degenerate n-type were examined at 300°K, 80°K, and 4.2°K. The spectra observed for all these types of GaSb are shown in Fig. 2 and 3. For p-type GaSb, a maximum with energy about 0.675 ev at 300°K and 0.774 ev at 80°K was observed with electrical injection. The spectrum obtained with optical injection showed a second maximum, ~ 0.715 ev at 300°K and ~ 0.80 ev at 80°K. These maxima are in the region where absorption coefficients are of the order of  $1000 \text{ cm}^{-1}$  so that the radiation can be strongly reabsorbed in the sample. In order to obtain the real spectrum, the observed spectrum should be multiplied by  $(1 + \alpha l)$  where  $\alpha$  is absorption coefficient and  $l$  is the diffusion length. This correction increases the emission at short wavelength, shifting slightly the peaks toward higher energy. This effect can be seen in Fig. 4 where corrected curves for the 80°K data were calculated using several different values of diffusion length. We estimated the true positions of the peaks to be about 0.73 ev at 300°K and 0.805 ev at 80°K. These energies are slightly higher than the energy gaps at the corresponding

temperatures. Apparently, the radiation is connected with direct hole-electron recombination. No radiation corresponding to the energy gap was observed at 4.2°K except for a weak trace observed on one sample.

The 0.775 ev peak at 80°K, 0.781 ev peak at 4.2°K, and the radiation with energy smaller than 0.71 ev at 300°K seem to be connected with impurities. The intensity of these radiations seemed to depend on the sample purity. As yet, there is no explanation for the peak corresponding to the energy 0.79 ev at 4.2°K.

The spectra for degenerate Zn-doped p-type look a little different. At each temperature, only one peak is observed. In the case of compensated, Te doped p-type, spectrum at 300°K looks similar to pure p-type; but at 80°K and 4.2°K, the short wavelength part of the spectrum is quite weak and all radiation seems to be connected with impurities. For degenerate, Te doped n-type with carrier concentration about  $10^{18} \text{ cm}^{-3}$  the short wavelength part of spectrum at 300°K is stronger than for the other types. It is possible that emission peak will shift after correction to an energy higher than in the case of pure p-type.

A more complete study of the different types of samples will be made. For all measured GaSb band to band transition seems to take place at room temperature with energy about 0.73 ev or higher.

Previously observed radiation by Braunstein<sup>1</sup> with peak about 0.625 ev and by the authors<sup>2</sup> with energy 0.675 ev appears to be the extrinsic property of the material. At low temperatures, extrinsic radiation seems to be stronger for all samples. At liquid helium temperature, some indication of direct hole-electron recombination was observed only on one sample.

The effect of different surface treatments on the recombination spectrum was studied for p-type material. The intensity of radiation is strongly dependent on surface treatment, but no significant differences in the shape of the emission spectra were found at 300°K and at 80°K.

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1. R. Braunstein, Phys. Rev. 99, 1892 (1955).

2. I. Filinski and H. Y. Fan, Semiconductor Research Second Quarterly Report. Jan. 1, 1961 to March 31, 1961.

#### Optical Behavior of Irradiated Silicon (A.K. Ramdas and H.Y. Fan)

The production rates of the oxygen dependent defects in silicon (11.98 micron and 11.56 micron absorption bands) have been investigated with 4.5 Mev electron irradiation of samples held at liquid nitrogen temperature (80°K). The 11.56 micron band is not observed in the sample when the sample was maintained at liquid nitrogen temperature. When it was warmed to room temperature, the absorption band appeared at a

strength comparable to what it would have been, had the bombardment been carried out at 0°C. This can be taken to be evidence that a defect, produced at the lower temperature, required motion to a suitable site, and this was possible at the higher temperature. The 11.98 micron band did not show such a simple behavior. It was produced at the lower temperature before warm up, and appeared to saturate at a level lower than what it would have been for a 0°C irradiation. Warm up to room temperature, produced an increase in the absorption band. Further work is in progress.

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A. K. Ramdas and H. Y. Fan, Semiconductor Research, First Quarterly Report, Oct. 1, 1960 to December 31, 1960.

Infrared Absorption in GaSb (E.J. Johnson and H.Y. Fan)

At low temperatures, a drop in absorption at about 17 microns is observed in p-type GaSb with Te present as compensating donor. Undoped GaSb does not display this drop at 80°K but shows a small drop at 200°K. These results seem to indicate that the acceptor in the material is a double center with a level at about .075 ev in addition to the known level at .025 ev.

Under high resolution, the absorption edge of undoped GaSb shows structure near liquid helium temperature. Three sharp peaks were observed along with a low energy tail. One peak at .8109 ev is probably due to the direct exciton corresponding to a binding energy of .002 ev.

Recent measurements have shown that at least the peak at the longest wavelength, 0.7965 ev, becomes more pronounced with decreasing temperature and that the peak is very sharp with a half-width of  $10^{-3}$  ev. Thus, it is unlikely that the absorption arises from the ionization of some impurity as it was postulated in the previous report. It is possible that the peak is due to exciton formation in the neighborhood of imperfections or due to the excitation of a deep lying donor.

Measurements of compensated samples show no resolvable peaks, but do show a more intense tail which extends to lower photon energy. The tail absorption is probably due to impurities, and its extension to longer wavelength is consistent with the 0.75 ev level indicated by the drop of absorption at 17 microns.

## II. IRRADIATION EFFECTS

### Paramagnetic Resonance in Neutron Irradiated Silicon (M. Nisenoff)

The resonance signal in neutron irradiated silicon depends on the position of the Fermi level after irradiation. A number of centers are seen when the Fermi level is near the middle of the forbidden gap. One of these centers has been studied in detail. It is observed in samples which have been irradiated at temperatures near 100°C and in samples which were irradiated at 50°C and subsequently annealed at 170°C for two hours. This center is stable against annealing at 500°C for up to 8 hours. Since this center is found in all samples regardless of impurity content, it is not associated with foreign atoms.

The resonance signal was studied in the temperature range from 4°K to 350°K. From the resonance data, it can be deduced that the resonant electron can be located at two possible positions in the defect. At 77°K and below, the electron is localized at one of the two equivalent positions. At these temperatures, the resonant electron is associated with only one silicon atom and the wave function is nearly axially symmetric with the axis of symmetry almost along the  $\langle 111 \rangle$  direction, the normal tetrahedral bond direction. As the temperature is raised above 77°K, the resonant electron begins to hop back and forth between the two equivalent positions, and by 160°K, the hopping is sufficiently rapid so that the electron is associated with both equivalent positions.

The simplest defect model which would satisfy the above resonance behavior would be a single isolated vacancy in which two of the four broken bonds have bridged over to form a saturated double bond and the two remaining broken bonds remain as localized orbitals. The center has a third electron which can be located on either of the localized dangling bonds. The main objection to this model is that a single isolated vacancy would probably not be stable enough to withstand the prolonged annealing that this center has received.

Another and possibly more likely model would be a divacancy - two vacancies in nearest neighbor lattice positions. One of the two dangling bonds would be located on a silicon atom adjacent to one of the vacancies and the other dangling bond would be located on a silicon atom adjacent to the second vacancy. The separation between these two silicon atoms is 4.50 Angstroms.

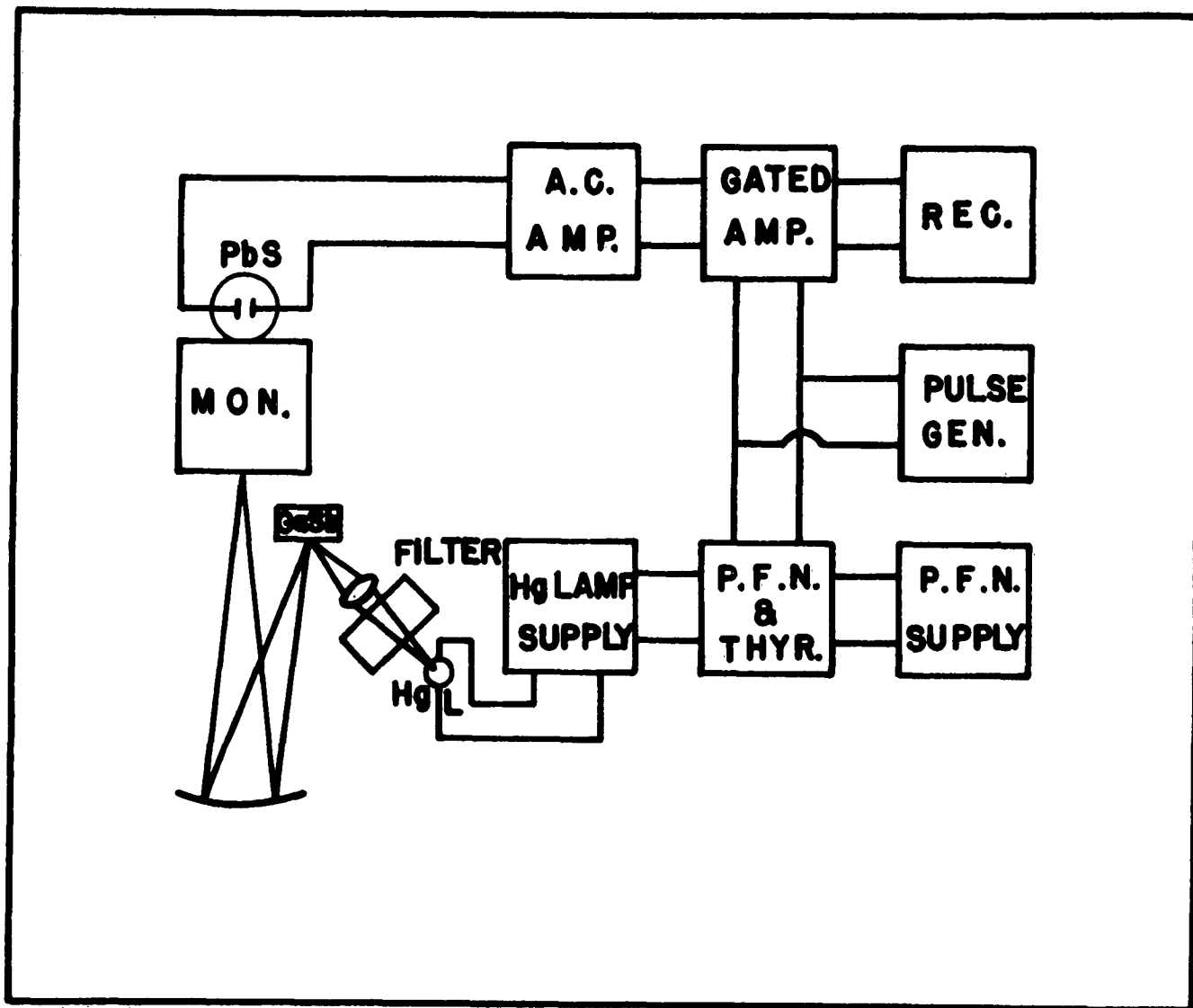


Fig. 1

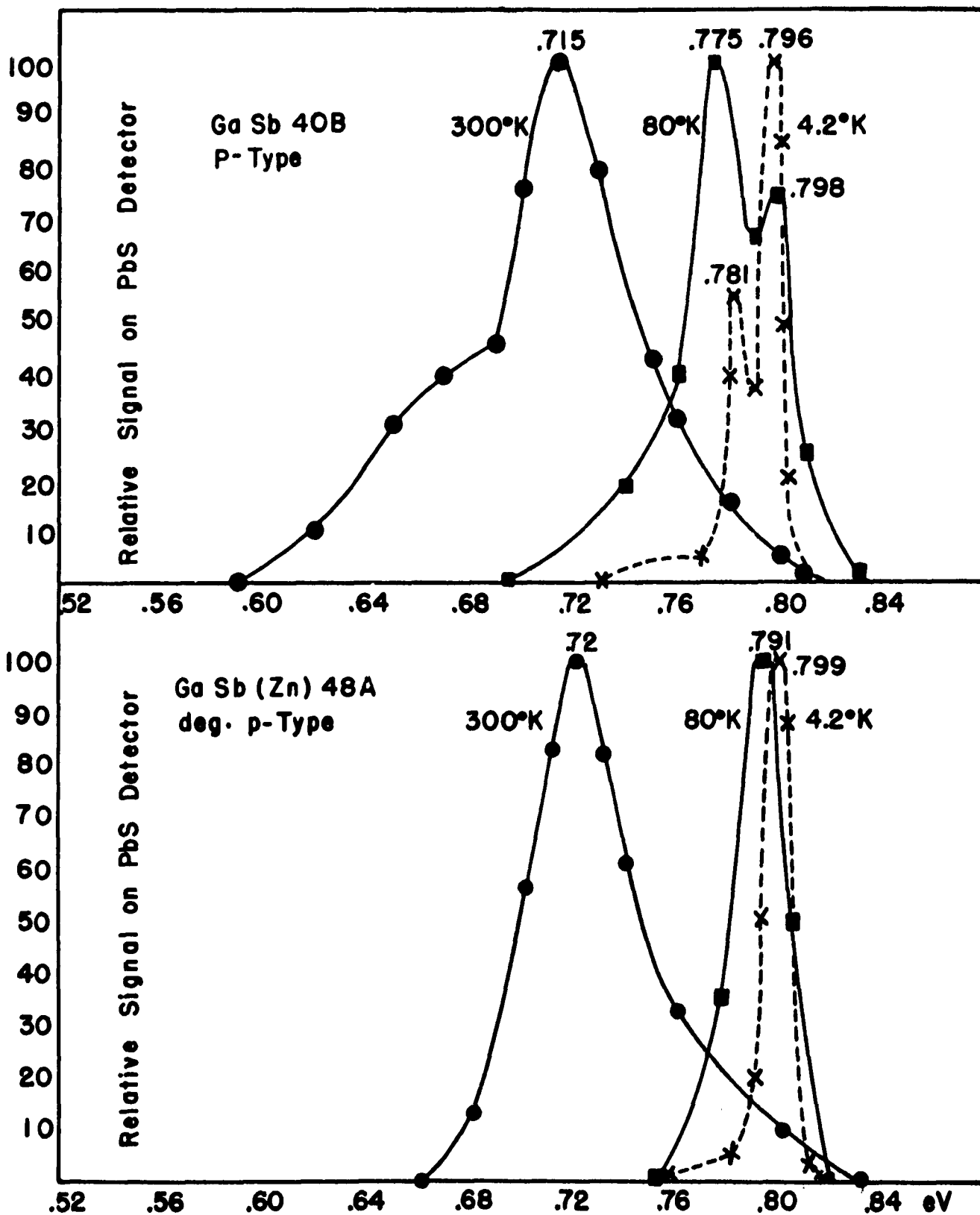


Fig. 2



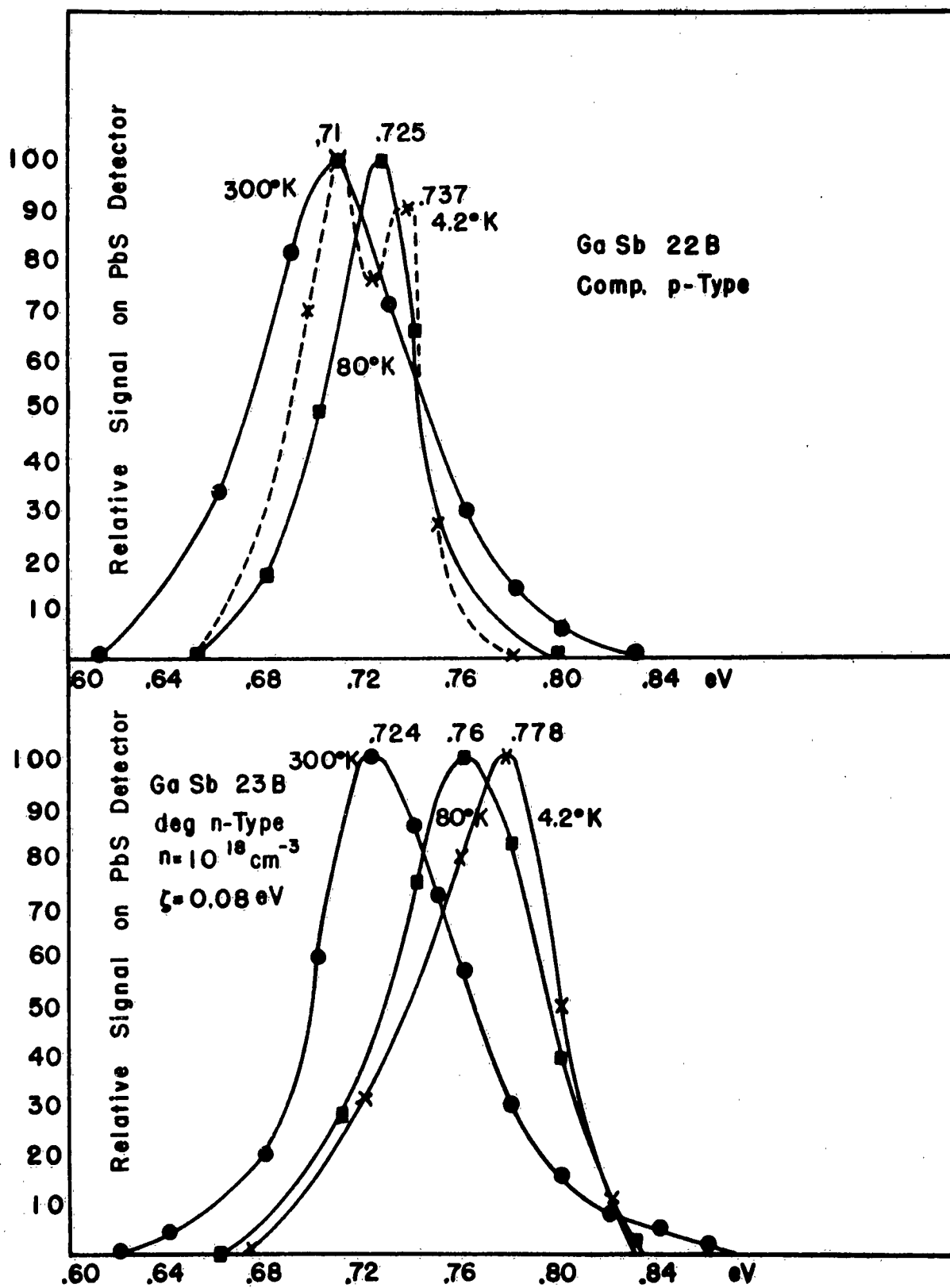


Fig. 3

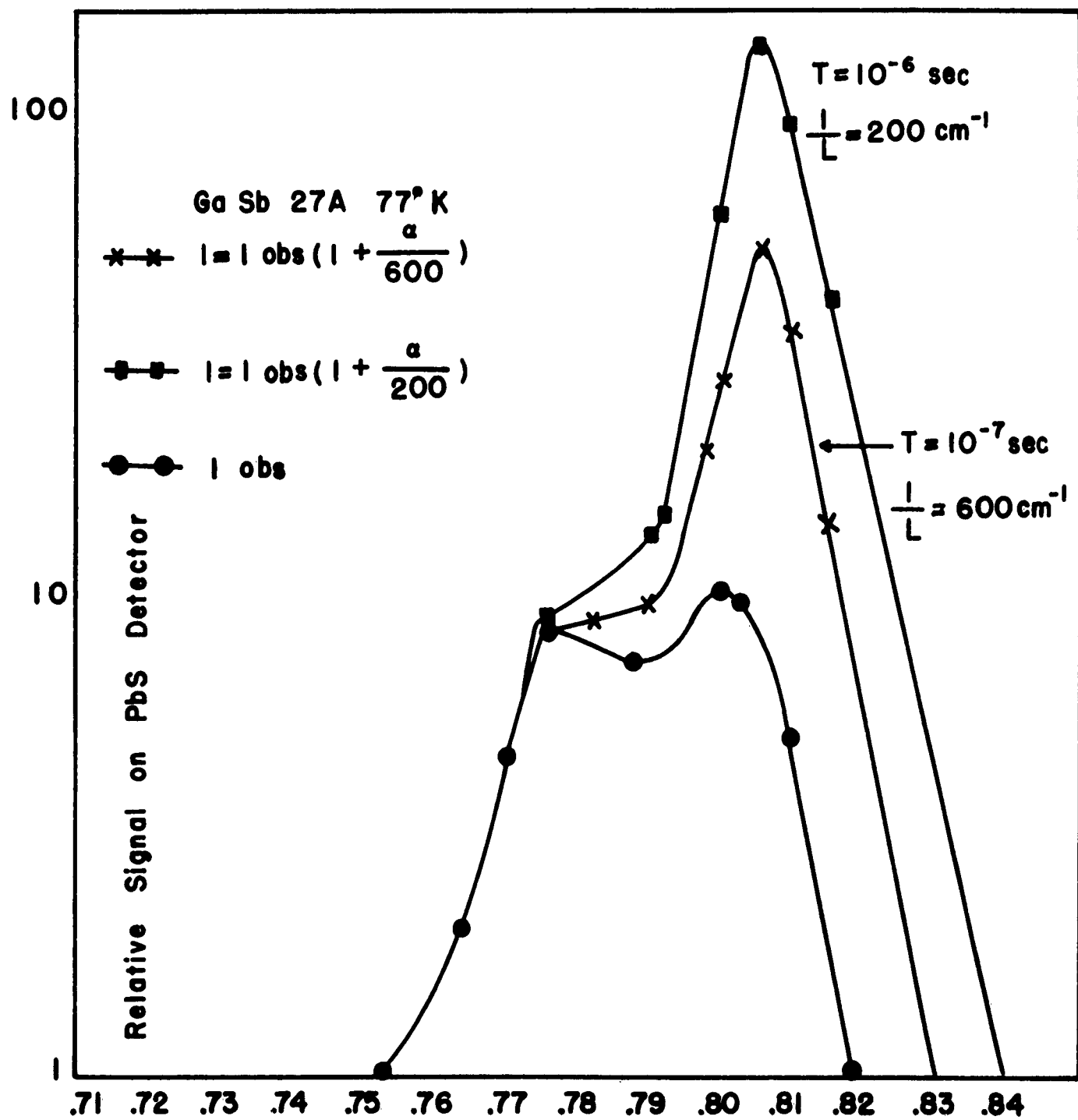


Fig. 4

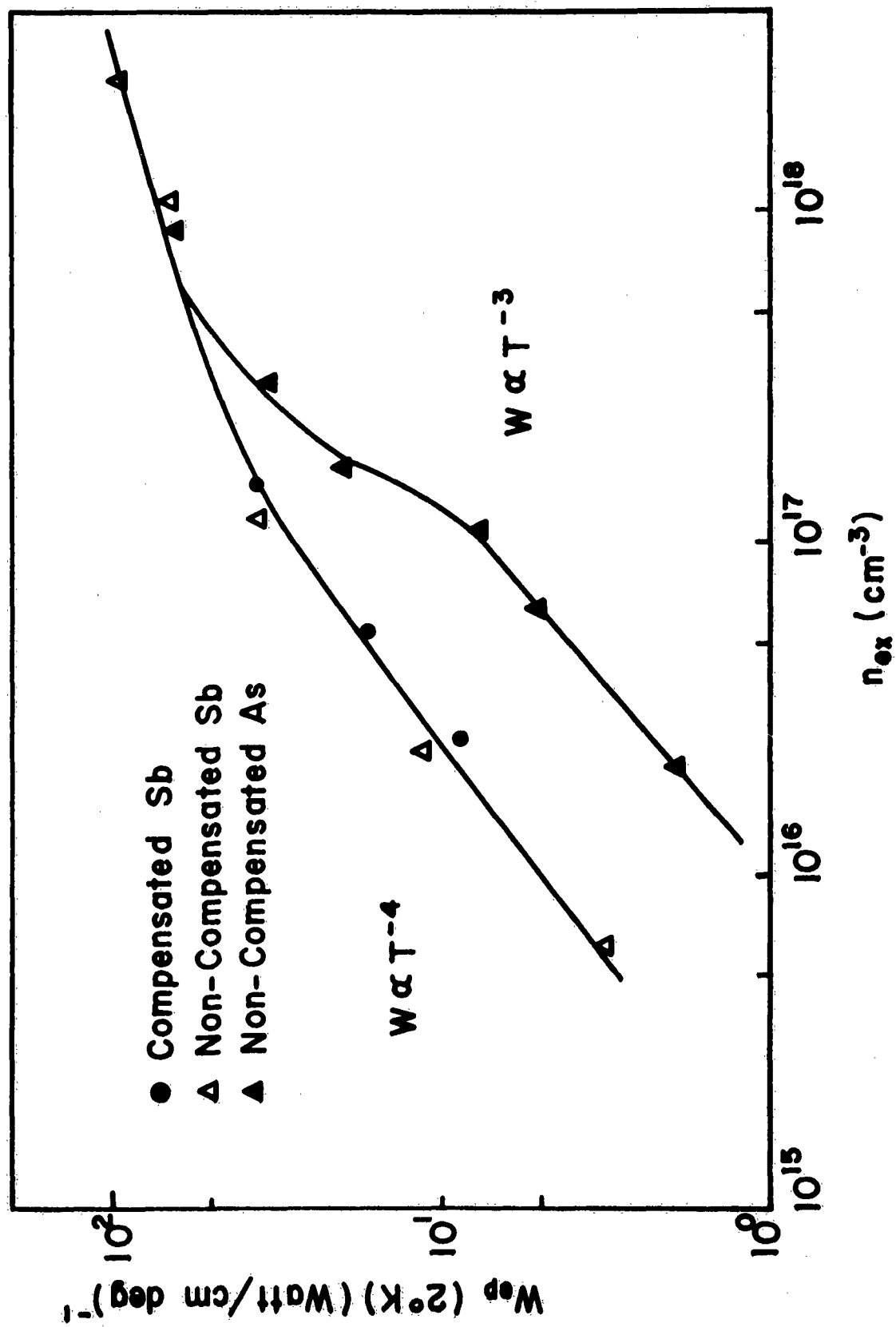


Fig. 5

A divacancy has been proposed by Watkins and Corbett<sup>1</sup> to explain two of the resonance signals seen in electron irradiated silicon. However, their divacancy model differs from the above one in that the resonant electron or electrons are associated with a different pair of silicon atoms. The separation between the silicon atoms in this model is 5.92 Angstroms.

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1. Watkins and Corbett, Private Communication.

Electron Paramagnetic Resonance - Silicon (W. Jung and G. Newell)

Pile irradiated silicon gives complex electron paramagnetic resonance spectra resulting from many magnetically active damage centers. Careful measurement of the angular variation of these spectra at 24 kMc provides just sufficient resolution to characterize the stronger centers by their individual g-tensors. Table I summarizes the information obtained this year. In all cases, the fermi level is at the center of the forbidden gap. Centers I, II, III, and the N center have been reported previously.

Center I was observed in small concentration in an arsenic containing sample heavily irradiated at  $\sim 100^{\circ}\text{C}$  [Westinghouse D-1009, crucible grown with  $10^{15}\text{ cm}^{-3}$  As,  $\phi = 1 \times 10^{19}$  nvt in Argonne reactor]. It has not been observed subsequently in undoped samples, but as these have all received smaller fluxes, the correlation of the center with arsenic is not conclusive.

Centers II and III are independent of impurity and are dominant in silicon irradiated at  $50^{\circ}\text{C}$ , accounting for 14 of the 16 strongest lines. An attempt was made to confirm the g-tensor assignment by differential saturation measurements at  $77^{\circ}\text{K}$ , but the combination of overlapping lines and difficult phase adjustments made the result unconvincing. Until analysis of the annealing data discussed below accounts for the remaining lines, the g-tensors must be considered provisional, although highly probable.

As indicated in table I, the g-values of  $77^{\circ}\text{K}$  showed only negligible shifts from the values at  $300^{\circ}\text{K}$ , indicating that these centers do not undergo a re-arrangement analogous to that of the N-Center in this temperature range.

The N center is dominant in samples irradiated at  $\sim 100^{\circ}\text{C}$  and is stable at  $500^{\circ}\text{C}$ . In one crucible grown sample [USSC No. 4,  $\phi = 5.5 \times 10^{18}$  nvt in the Argonne reactor] one hour at a temperature between 500 and  $550^{\circ}\text{C}$  destroyed the N center and replaced it by Center IV together with some unidentified weaker lines.

Center IV strikingly resembles the N center in showing the accidental (?) degeneracy which gives rise to a single resonance line in the  $\langle 100 \rangle$  direction. In Center IV, this line actually appears to be an overlapping doublet split by about

Table I

Center	$T^{\circ}K$	g tensor (1)			$\theta$	Production Temp. (1 hr.)	Annealing Temp. (1 hr.)	Impurity Dependence
		$g_1$	$g_2$	$g_3$				
I	300	$\pm 0.0002$	$\pm 0.0002$	$\pm 0.0002$	$\pm 0.5$	Present after Bombardment at $\sim 100^{\circ}C$	?	Possibly As
II	300 77	2.0109 2.0110	2.0125 2.0119	1.9971 1.9968	15.0° 14.8°	Present after Bombardment at $\sim 55^{\circ}C$	170°C	Independent
III	300 77	2.0010 2.0006	2.0070 2.0069	2.0127 2.0124	32.2° 32.5°	Present after Bombardment at $\sim 55^{\circ}C$	170°C	Independent
IV	300	2.0088	2.0113	2.0050	22.0°	500 - 550°C	< 700°C	Probably independent; Oxygen not excluded.
N	300 77	2.0083 2.0113	2.0114 2.0125	2.0035 2.0030	19.3° 32.5°	170°C	500 - 550°C	Independent

(1) The  $g_2$  axis is parallel to  $\langle 110 \rangle$ ;  $g_1$  lies in the plane containing  $\langle 001 \rangle$  and  $\langle 110 \rangle$  making an angle  $\theta$  with  $\langle 001 \rangle$ .

twice experimental error; nevertheless, the two g-tensors are markedly similar, differing well beyond experimental error only in the value of  $g_3$ . The two centers are probably related structurally and suggest the possible existence of a family of N type centers.

#### A. Isochronal Anneal

To confirm the isolation of centers II and III, and to study their relation to the production of the N center, a series of isochronal anneals has been carried from 90°C to 170°C in 10 degree steps, and from 175°C to 185°C in 5 degree steps.

Ruby is found to be an excellent intensity standard for these experiments. By orienting the c-axis parallel to the axis of rotation of the magnet, a line is obtained which is independent of magnet position and, at  $g = 2.0741$ , is conveniently displaced from the spectra of interest. The broad line (15.7 gauss peak to peak) permits a weighable crystal to be used; 1.79 mg of 0.1% ruby containing  $\sim 2 \times 10^{16}$   $\text{Cr}^{+++}$  mounted in the cavity opposite the sample gives a signal comparable to the strongest sample resonance.

Detailed analysis of this data is in progress, but the following conclusions can be drawn from a qualitative inspection:

(1) Above 160°, the annealing rate of Centers II and III and the growth of new centers increases rapidly. There is a tentative indication that some new centers grow in slightly before the N center.

(2) After the 11th step (175°, 30 min.) of annealing, Center III has almost completely disappeared while center II is barely detectable. This indication of differential annealing must be verified by more complete analysis.

(3) The EPR spectrum after the last step (185°) of annealing is qualitatively similar to that of samples irradiated at  $\sim 100^\circ\text{C}$  (N center dominant). The formation of the N center during the annealing process appears to be confirmed.

The almost simultaneous change of several centers suggests a common mechanism which may be significant to the understanding of radiation damage. To supplement the isochronal data and help throw light on the activation energies and orders of the reactions, a set of isothermal annealing experiments is planned.

#### B. Apparatus

The 24 kMc superheterodyne spectrometer built for this work is novel primarily in its frequency control circuits. The frequency error signal is derived from the main klystron input by a resonant cavity bridge and detected in a phase sensitive superheterodyne system almost identical to that used in the signal channel. The two channels use the same local oscillator, and the I.F. modulation characteristic of the Pound I.F. stabilizer is omitted. The local oscillator is slaved to the main klystron

by phase locking the beat frequency (I.F.) to a 25 Mc crystal oscillator. Enough of the circuits are transistorized to give a 50% saving in bulk and power supply requirements.

A rough measurement showed the sensitivity to be within about a factor of ten of theoretical and ample for initial work. Increasing demands on sensitivity are now beginning to make a thorough investigation of this noise figure desirable.

#### Electron Paramagnetic Resonance (D. Trueblood and G. Newell)

Electrical measurements by another group on germanium which has been irradiated with electrons at 77°K shows the presence of long lived traps which may be filled by white light or by high voltage pulses, or emptied by infrared irradiation. To investigate this system, we are building an x-band super heterodyne E.P.R. spectrometer together with a cryostat which will permit both irradiation and measurement at liquid nitrogen or liquid helium temperature.

The spectrometer is being designed around a commercial stabilized oscillator (LFE Model 814), but otherwise resembles the 24 kMc system previously constructed. The cryostat and most of the circuits have been built and are now being tested.

The high dielectric constant of germanium combined with the expected photoconductivity of the sample requires a special cavity design. A cylindrical cavity operating in the  $TE_{011}$  mode will be used with the sample in the form of a rod along the axis. The diameter of the sample must be small to keep the lossy material in a region of low electric field. With air in the rest of this cavity, the boundary conditions at the dielectric interface operate to exclude the R.F. field from the sample and unduly reduce the filling factor. Filling the cavity with low loss silicon greatly diminishes this effect and at the same time reduces the dimensions of the cavity to a convenient value. As no R.F. current crosses the cylindrical junction, a loose fit which permits easy manipulation of the sample at low temperature is permissible. A calculation of the expected filling factor has been made and shows the configuration to be satisfactory.

#### Cyclotron Resonance - 5 mm Apparatus (T. Tohver and G. Newell)

A microwave bridge system has been designed for studying cyclotron resonance in semiconductors at 56 kMc ( $\lambda = 5$  mm), and such items as helium dewars and test cavities have been built. The major effort in the last quarter has been devoted to the 100 Kc "jitter" frequency stabilization circuit. The high operating voltage ( $\sim 3000$  volts) of the 5 mm klystron led to a number of sources of corona discharge noise, each of which has now been located and remedied.

### III. LOW TEMPERATURE STUDIES

#### Heat Capacity of Several Superconductors and Other Solids at Very Low Temperatures

(C.A. Bryant and P.H. Keesom)

The heat capacities of rhenium, indium, and tin have been measured between  $1/3$  and  $4\frac{1}{2}^{\circ}\text{K}$  in the normal and superconducting states. Motivation was chiefly to determine the temperature dependence of the superconducting electronic specific heat  $C_{es}$  as far down as possible, comparing the result with the theory that should have the form  $A \gamma T_c \exp(-bT_c/T)$ , where  $\gamma T$  is the normal electronic term and  $T_c$ , the transition temperature. Assuming the normal and superconducting lattice terms to be equal and of the form  $\alpha T^3 + \beta T^5 + \mu T^7$ ,  $C_{es}$  was considered to be the superconducting specific heat minus the normal lattice term. However, in the case of rhenium, there was found an anomalous contribution  $A_0 T^{-2}$  due to the nuclear electric quadrupole moment of the Re interacting with the crystalline field. The constant parameters in the specific heat were:  $\gamma = 2.31 \pm .04$  millijoule/mole  $\text{deg}^2$ ,  $\alpha = 0.027 \pm .004$  millijoule/mole  $\text{deg}^4$  (corresponding to a Debye temperature  $\theta = 4.7 \pm 20^{\circ}\text{K}$ ),  $A_0 = 0.052$  millijoule  $\text{deg}/\text{mole}$  (corresponding to RF resonance frequencies of 42 and 84 Mc)  $1.70^{\circ}\text{K}$  (the transition was quite broad, continuing until  $1.83^{\circ}\text{K}$ ).

The salient feature in the results on indium was a superconducting specific heat less than the normal lattice term below  $0.8^{\circ}\text{K}$ , around 30% less at  $0.37^{\circ}\text{K}$ . This conflicts with the assumption of equal normal and superconducting lattice terms unless there exists a negative contribution in the superconducting state. Accounting for a small nuclear quadrupole specific heat,  $9 \times 10^{-4} T^{-2}$  millijoule/mole  $\text{deg}.$ , it was found that (for one sample) the normal specific heat  $C_n$  could be represented as  $(1.59 \pm .02) T + (1.53 \pm .03) T^3 + 0.008 T^5 + (9 \times 10^{-4}) T^{-2}$  millijoule/mole  $\text{deg}.$ ,  $0.35 < T < 4.5^{\circ}\text{K}$ . The Debye temperature corresponding to the  $T^3$  part of the lattice term is  $\theta = 108^{\circ}\text{K}$ . With the choice of  $a = 11$  and  $b = 1.5$  in the expression for  $C_{es}$ , the superconducting specific heat became expressible as  $59.5 \exp(-1.6 T_c/T) + 1.72 \exp(-0.051 T_c/T) T^3 + (9 \times 10^{-4}) T^{-2}$  millijoule/mole  $\text{deg}.$ ,  $T < 0.7 T_c$ . The first term is  $C_{es}$ ; the third, the nuclear quadrupole term; and the second, everything left over, expressed as a modified  $T^3$  lattice term. In contrast, the specific heat of tin could be represented in the usual way, with equal normal and superconducting lattice terms:  $C_n = \gamma T + \alpha T^3 + \beta T^5 + \mu T^7$  and  $C_s = \alpha \gamma T_c \exp(-bT_c/T) + \alpha T^3 + \beta T^5 + \mu T^7$ , with  $\gamma = 1.80 \pm .02$ ,  $\alpha = 2.42 \pm .04$  ( $\theta = 200^{\circ}\text{K}$ ),  $\beta = 0.0040$ ,  $\mu = 0.00014$ ,  $a = 7.63$ , and  $b = 1.41$ ; all of these are in millijoule units. Magnetic measurements give  $T_c = 3.714^{\circ}\text{K}$ , but the specific heat discontinuity appeared at  $3.701^{\circ}\text{K}$ ; the difference has not been satisfactorily explained. Thermodynamic calculations of the critical magnetic field at



$0^{\circ}\text{K}$ ,  $H_0$ , yielded 284 oe. for In and 306 oe. for Sn. In the case of tin, critical field  $H_c(T)$  was less than  $H_0 [1 - (T/T_c)^2]$  for all  $T < T_c$ , as found in most superconductors; but for indium the deviation of  $H_c(T)$  from this parabolic form was negative only down to  $0.8^{\circ}\text{K}$ , and positive below this temperature.

Measurements above  $1^{\circ}\text{K}$  of two molybdenum specimens (nonsuperconducting) resulted in  $\gamma = 1.91$  and  $1.93 \pm .02$  millijoule/mole deg., and  $\theta = 458 \pm 15^{\circ}\text{K}$ .

Results on superconducting Mo-Rh alloys are reported, but remain inconclusive because of the difficulty of determining the concentration of Rh and the nonuniform composition.

The contribution by 0.09% manganese to the specific heat of silver did not reveal the expected maximum in  $C/T$  above  $0.35^{\circ}\text{K}$ , the lowest temperature measured. Although a Schottky type specific heat is expected from reorientation of the electron spins on the Mn ions in some local magnetic field, the high temperature tail of the specific heat contribution does not have a  $T^{-2}$  dependence below  $3^{\circ}\text{K}$ . This was interpreted to mean either that the local magnetic field at the Mn ions must be the order of  $10^3$  oe., which is unbelievably large, or that some other cooperative effect exists among the Mn ions which produces a contribution in addition to the Schottky term.

The specific heat of pure germanium could be specified below  $4^{\circ}\text{K}$  by  $\alpha = 0.0380 \pm .0005$  millijoule/mole deg.<sup>4</sup>, corresponding to  $\theta = 371 \pm 2^{\circ}\text{K}$ . The electronic specific heat,  $T$  and  $\theta$  were also reported for several samples of degenerate N type germanium. It was found that as impurities were added,  $\theta$  decreased to as low as  $363^{\circ}\text{K}$  for  $0.47 \times 10^{19} \text{ cm}^{-3}$  arsenic in the sample. As expected,  $\gamma$  increased as the conduction band filled with electrons, allowing the calculation of effective mass and Fermi energy on the basis of the oversimplifying assumption of a parabolic-shaped conduction band, neglecting the influence of the impurity band on the distribution of energy states.

Superconducting Niobium Solenoid (P.H. Keesom and B.J.C. van der Hoeven, Jr.)

In measuring the specific heats of various superconductors on the  $\text{He}^3$  cryostat, magnetic fields up to 1000 gauss are necessary for quenching the superconductivity of these metals. Formerly, an electromagnet, having a gap of 16 cm, was placed externally around the 15 cm diameter outer dewar. The possibility of using a smaller, persistent current, superconducting niobium magnet around the 8 cm diameter outer can, immersed in liquid  $\text{He}^4$ , has been investigated.

A trial solenoid 1 1/2 inch long and inner diameter 1/2 inch was wound with 0.005 inch diameter, silk insulated, niobium wire, having 110 turns/cm.<sup>1</sup> The two ends of the coil were spot welded. Platinum leads of 0.02 inch diameter were spot welded to the two niobium leads 5 cm away from the shorting weld, and copper leads soft soldered to the platinum for current input.

A persistent current of 4.0 amperes was trapped, the resultant field of 550 gauss being measured by flip coil methods. A similar solenoid with 300 turns/cm is planned for use around the outer can.

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1. S. H. Autler, Revs. Sci. Inst. 31, No. 4, 369 (1960).

Magnetic Susceptibility (D.H. Damon and A.N. Gerritsen)

The magnetic susceptibility of n-type germanium with donor concentrations between  $10^{16} \text{ cm}^{-3}$  and  $2 \times 10^{17} \text{ cm}^{-3}$  was measured in order to investigate the interactions between donors. The measurements were made between  $4.2^\circ\text{K}$  and  $1.35^\circ\text{K}$ . The susceptibility of antimony-doped germanium has been contrasted with that of arsenic-doped germanium.

The measurements have been made by the Faraday method. A sensitive microbalance and a low temperature cryostat have been constructed with which to perform these measurements. At low temperatures, the motion of the heat exchange gas, initiated by temperature gradients, interferes with the measurements and limits their accuracy.

Sonder and Schweinler have proposed that, for moderate donor concentrations, pairs of donors be treated as quasi-hydrogen molecules. The results of this investigation show that the molecular theory predicts the observed temperature dependence of the susceptibility of the extrinsic electrons for appropriate donor concentrations. The antimony-doped samples exhibit a stronger donor interaction and a larger orbital diamagnetism than the arsenic-doped samples, consistent with the hydrogenic model.

For equal donor concentrations in the neighborhood of  $10^{17} \text{ cm}^{-3}$ , the susceptibility of antimony-doped germanium is considerably more diamagnetic than the susceptibility of arsenic-doped germanium. The susceptibility of these samples increases very rapidly with donor concentration. An empirical relation between the susceptibility of arsenic and antimony-doped germanium has been found. These observations suggest that the extrinsic electrons should be regarded as localized below  $4.2^\circ\text{K}$  for donor concentrations less than or equal to  $10^{17} \text{ cm}^{-3}$ .

Impurity Conduction in Sb-Doped Germanium (G. Sadasiv)

An adiabatic demagnetization cryostat has been constructed for measuring the electrical resistivity of samples at temperatures down to  $0.1^\circ\text{K}$ .

Measurements have been made on four Sb-doped germanium samples which have room temperature Hall coefficients between  $-44$  and  $-77 \text{ cm}^3 \text{ coulomb}^{-1}$ .

Fritzsche<sup>1</sup> has characterized the impurity conduction in similar samples at helium temperatures by an activation energy given by

$$\rho = \rho_0 \exp (\epsilon_3/kT)$$

$\epsilon_3$  being dependent on the impurity concentration.

A semi-log plot of  $\rho$  against  $1/T$  shows that this description is not valid over any wide range of temperature; the slope of the line gradually decreases as  $1/T$  increases.

The impurity conduction in these samples, therefore, seems to be similar to that observed in silicon samples with a high impurity concentration.<sup>2,3</sup>

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1. H. Fritzsche, J. Phys. Chem. Solids 6, 69 (1958).
  2. T. A. Longo, R. K. Ray, and K. Lark-Horovitz; J. Phys. Chem. Solids 8, (1959).
  3. G. A. Swartz, J. Phys. Chem. Solids 12, 245 (1960).

Transport Properties of N-Type Germanium at Low Temperatures (J.F. Goff and N. Pearlman)

A. Introduction

The data which have been presented in these progress reports over the last two years have been analysed and presented in Goff's thesis. This analysis will be given in fair detail in a forthcoming paper. Here the principal conclusions derived from this investigation will be summarized.

B. Thermal Conductivity

It has been shown that one of the effects of excess electrons  $n_{ex}$  (the concentration of donors less that of the acceptors) is to limit the thermal conduction. At temperatures below that of the thermal conductivity maximum, it has been definitely proven that the thermal conductivity is reduced by these electrons by measuring compensated, heavily doped, Ge samples; while at higher temperatures the decrease of the thermal conductivity appears to be correlated with the presence of electrons in the conduction band since compensated samples with the same  $n_{ex}$  but with a faster freezeout rate than non-compensated samples have a higher conductivity. It has been shown that the scattering of phonons by electrons must be of at least two kinds: one for electrons in well formed bands where the electron propagation vector is a good quantum number and another for electrons in semi-isolated impurity states. These classes can be seen in Fig. 1 where the thermal resistivity at 2°K,  $w(2^{\circ}K)$ , is plotted against  $n_{ex}$  (the boundary resistance has been subtracted for all samples). From the behavior of the electrical resistivity, it appears that the electron states of the As atoms have not completely merged with the conduction band even at concentrations of  $3 \times 10^{17} \text{ cm}^{-3}$ .

The first case applies to Ge with non-compensated carrier concentrations of the order of  $1 \times 10^{18} \text{ cm}^{-3}$  down to the lowest temperatures measured. In this case, there seems to be no dependence upon impurity species. Calculations in which the relaxation time for phonons interacting with electrons as derived by Ziman<sup>1</sup> is included in the thermal conductivity integral in the Callaway model<sup>2</sup> indicate that the theory of

electron-phonon interaction is not complete because it does not explain the thermal conductivity even at low temperatures where there is no question that it is limited by electrons. It is suggested that one would expect correction terms to this integral because the electron-phonon interactions considered conserve energy and crystal momentum, as do the N-processes that introduce correction terms in Callaway's model. It is hoped that these new correction terms will be of the proper sign and magnitude to increase the effect of electrons on phonons throughout the temperature range measured.

In the second case where the electrons are in semi-isolated, neutral, donor states, the thermal resistivity depends upon the impurity species contributing the electron. Keyes<sup>3</sup> has shown that a model developed by him gives a semi-quantitative fit with these data. However, his model does not explain the different slopes observed for the temperature dependence of this resistivity at low temperatures for the As and Sb impurities.

It would seem possible to explain these different slopes phenomenologically by assuming that the electron-phonon interaction of an electron in an As impurity state interacts with higher energy phonons than does an electron in an Sb impurity state and by including this interaction in the Callaway integral. This suggestion is in qualitative agreement with the prediction of the Keyes model that since As is a smaller atom than is Sb, it will interact with shorter wavelength phonons.

In brief, these data seem to be qualitatively compatible with the Keyes model, in particular, the major supposition that the interaction of phonons with electrons in semi-isolated states involves virtual electron excitation rather than transition to levels on adjacent impurity atoms.

#### C. Effect of Compensation on the Impurity Band

These experiments give considerable evidence that for donor concentrations of about  $10^{18} \text{ cm}^{-3}$ , compensation of the order of 80% or more changes the impurity band structure in Ge. These observations are summarized:

(1) The Hall coefficient for the compensated sample shows a temperature dependence in the temperature range from 77 to 400°K that indicates that the carrier concentration in the conduction band  $n$  is a function of temperature. At these concentrations, if either impurity species Sb or Ga were in the crystal singly,  $n$  would be constant.

(2)  $n(T)$  has been calculated from the simple charge equality condition in which an ionization energy is assumed. The agreement of the calculation with the data is reasonable.

(3) Even at low temperatures, the electrical resistivities of the compensated samples do not show the temperature-independent behavior associated with degeneracy but rather increase as  $T$  is decreased. This behavior is generally associated with electrical conduction between semi-isolated states.

(4)  $Q_p$ , the phonon-drag component of  $Q$ , on the compensated samples agrees with the values found for non-compensated samples with the same  $n_{ex}$ . Since  $Q_p$  is found from  $Q$  by computing  $Q_e$ , the electronic component, with the  $n(T)$  values discussed in point 1, this result is consistent with point 1. Further, the fact that the magnitude of  $Q$  (SbGa 204) is greater than that of  $Q$  (Sb 207) seems to indicate that the neutralization rate is greater for the compensated sample than for the non-compensated one.

(5) The equality of the thermal conductivity of the compensated and non-compensated samples with the same  $n_{ex}$  and majority impurity seems to indicate that the impurity atoms contributing to the resistivity (Keyes model) are in the same type state.

It is not likely that these impurity states are due to the random arrangement of the impurity atoms because the possibility that an impurity atom in the compensated samples  $N_{DC}$  is as far from its neighbors as it is in a non-compensated sample with the same  $n_{ex}$  (donor concentration  $N_{DN}$ ) is  $\exp(-N_{DC}/N_{DN})$ . Thus in the case of SbGa 204 and Sb 207 where  $N_{DC} = 10^{18} \text{ cm}^{-3}$  and  $N_{DN} = 10^{16} \text{ cm}^{-3}$ , the probability of finding an isolated atom is  $\exp(-100)$ . It appears rather that compensation actually reinstates the impurity levels into the energy gap. This conclusion seems compatible with the calculation of Lehman and James<sup>4</sup> that the ionization energy of impurities depends markedly upon the carrier concentration.

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1. J. M. Ziman, Phil. Mag. 1, 191-198 (1956). See also "Corrigendum" Phil. Mag. 2.

2. J. Callaway, Phys. Rev. 113, 1046-1051 (1959).

3. R. W. Keyes, Phys. Rev. 122, 1171-1176 (1961).

4. G. W. Lehman and H. M. James, Phys. Rev. 100, 1698-1712 (1955).

#### Germanium Resistance Thermometers (N. Pearlman and M.P. Mathur)

An attempt to use germanium as a suitable low temperature thermometer was made in this laboratory. Previously, carbon resistors were used for such temperature measurements. But these carbon resistors were found to suffer from two main defects:

(i) Their lack of reproducibility in reading on successive cycling of temperature from room temperature to helium temperatures.

(ii) Their low sensitivity above about 50°K.

To overcome these defects several alloyed Ge-single crystals were tried out. The germanium thermometers (cross section about a few tenths of millimeter square and length 2-6 mm) were glued on a copper plate and were found to be quite unaffected by successive coolings from room temperature. Heavily doped n-type Ge sample prepared by Roth and reported earlier by Pearlman and Goff on their thermal conductivity measurements was found to be a suitable material for Ge thermometers. The calibration curves showed the reproducibility of these thermometers within the sensitivity of measurement (4 significant figures in resistance) on temperature cycling between 300°K and 4°K. Later on a D.C. microvoltmeter was employed to increase the sensitivity of the measurements. Demounting the thermometers from the plate, removing their lead wires, and resoldering them did not seem to affect the reproducibility. Thermometers show no dependence of resistance on power for dissipation as high as  $5\mu\text{w}$  at 4°K and  $0.5\mu\text{w}$  at 1.2°K. In this temperature range,  $dP/dT$  varies from  $1-10 \times 10^{-4}$  watts/deg. K.

#### Piezo-Thermal Conductivity Effect in Ge (R.J. Sladek)

The interpretation of previously obtained experimental results<sup>1</sup> on the piezo-thermal conductivity of pure and lightly doped germanium at liquid helium temperatures was made in collaboration with R. W. Keyes (with whom a joint scientific paper was written and submitted to the Physical Review). Theory was developed for the influence of applied static stress on the perturbation energy involved in the scattering of phonons by donor electrons making virtual transitions. Predictions of this theory account for the sign and magnitude of the large changes in thermal conductivity produced by (111) or (110) tension in Sb doped samples as well as for the absence of a large effect due to (100) tension in these samples or due to any type of tension in pure or As doped samples.

Preparations for further experimental investigation have almost been completed.

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1. R. J. Sladek, Bull. Am. Phys. Soc., Ser. II, 6, 175 (1961).

#### IV. GENERAL

##### Shallow Acceptor States in Germanium (H.M. James and K.S. Mendelson)

Calculations of absorption coefficient and Zeeman splitting were made for shallow acceptor states in germanium. Poor agreement of the results with experiment indicated that the wave functions used in the calculation were inadequate. A calculation is, therefore, being made to obtain improved wave functions. A variational solution of the effective mass equation, in the limit of very strong spin-orbit coupling, is being tried, using trial functions in which the angular dependence is determined by symmetry conditions and the radial dependence is left in terms of unknown functions. The variational procedure then leads to a system of differential equations for these functions. Some progress has now been made in solving these equations.

##### Recombination of Electrons and Donors in n-Type Germanium (S. Rodriguez)

A calculation was made of the recombination cross section of an electron having a spherical effective mass and a donor impurity whose bound states can be described by a hydrogenic model. The recombination takes place with an initial capture of the electron in an excited state of the donor center with the emission of a phonon followed by successive transitions to lower lying states with emission of phonons. The calculated cross section agrees with the experimental one by a factor of the order of unity. The agreement between the temperature dependence of the calculated and the experimental recombination cross sections is good. Also, we obtain a small but significant dependence of the recombination cross section on the binding energy of the ground state of the donor.

##### Hall Coefficient Expression in Anisotropic Crystals (V.A. Johnson)

In order to interpret Hall effect measurements in single crystal tellurium, it is necessary to have a Hall coefficient expression that is valid for anisotropic material. This expression should not be based upon specific assumptions about the type of scattering encountered by the charge carriers or about the position of the Fermi level (i.e. degree of degeneracy of the carriers). Such an expression has been derived subject to the restrictions: (1) weak magnetic field approximation; this means that terms containing  $H^2$  or higher order of  $H$  were neglected, (2) the principal axes of the mass tensors coincide with the crystal axes, (3) the directions of current flow, magnetic field, and Hall field are mutually orthogonal and coincide with the principal axes of the mass tensors, and (4) anisotropy in the transport processes is given by the anisotropy of the mass tensors and need not be considered separately in the relaxation times.

Assume that two kinds of charge carriers are present in the sample; denote these by the subscripts a and b. Let  $q_a$  and  $q_b$  represent the respective charges,  $\tau_a, \tau_b$  the respective relaxation times associated with the scattering encountered by the carriers, and  $f_o^a$  and  $f_o^b$  the respective unperturbed distribution functions. Then, in Gaussian units, the Hall coefficient becomes

$$R = - \frac{16\pi\sqrt{2}}{3h^3c} \frac{\left\{ q_a^3 \frac{\sqrt{m_1^a m_2^a m_3^a}}{m_1^a m_2^a} \int_0^\infty \tau_a^2 \epsilon \sqrt{\epsilon} \frac{\partial f_o^a}{\partial \epsilon} d\epsilon + q_b^3 \frac{\sqrt{m_1^b m_2^b m_3^b}}{m_1^b m_2^b} \int_0^\infty \tau_b^2 \epsilon \sqrt{\epsilon} \frac{\partial f_o^b}{\partial \epsilon} d\epsilon \right\}}{\sigma_1 \sigma_2},$$

$$\text{where } \sigma_1 = n_a |q_a| \mu_1^a + n_b |q_b| \mu_1^b$$

$$\sigma_2 = n_a |q_a| \mu_2^a + n_b |q_b| \mu_2^b.$$

Here  $n_a$  and  $n_b$  are the carrier concentrations and the  $\mu$ 's are the mobilities of the two kinds of carriers in directions 1 and 2; the various  $m$ 's are the components of the diagonalized mass tensors. The subscript 1 applies to mass values and mobilities in the current direction, subscript 2 to the direction of the Hall field, and subscript 3 to the magnetic field direction.

When classical statistics are assumed and the scattering is attributed either to lattice scattering alone or ionized impurity scattering alone, the general expression above can be reduced to the simpler formulas that have been discussed in the past.

#### Material Preparation (K. Masumoto and L. Roth)

Large crystals of ZnSb have been obtained by the Bridgman method. These crystals have been identified and oriented by x-ray analyses performed by H. J. Yearian and will be used as seeds for growing single crystals by the Czochralski technique.

Preliminary measurements show a resistivity at room temperature of 0.46 ohm-cm and Hall coefficient of + 56.6. At 78°K,  $\rho = 0.13$  ohm-cm and  $R = + 79.4$  were obtained.

Work has continued on the preparation of single crystals of Ge, GaSb, and InSb with various combinations and concentrations of impurities.



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PERSONNEL WORKING ON PRF 2641  
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